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STUDIES IN THE METALLURGY OF BERYLLIUM

BY

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THESIS

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY  
SUPERVISION BY OTTO ERSKINE HUNTLEY  
ENTITLED STUDIES IN THE METALLURGY OF BERYLLIUM

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR  
THE DEGREE OF MASTER OF ARTS

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\*Required for doctor's degree but not for master's



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## INTRODUCTION



## I. OBJECT.

The object of this investigation was to study the metallurgy of beryllium with a view to the discovery of a method that would prove successful on the large scale. The plan suggested was to carry out the investigations on a small scale and if a successful method was discovered, to try it out on a large scale.

The difficulty which is encountered in the extraction of beryllium from beryl has kept beryllium in the category of "rare" elements altho beryllium bearing minerals occur extensively. When a method is proposed by which beryllium can be prepared cheaply an adequate supply of the mineral will be available.<sup>(1,3)</sup>

Beryllium possesses properties which make it useful for the manufacture of special electrical and other scientific instruments and apparatus; its alloys with copper are known to possess sonorous properties; its salts are useful in the synthetic preparation of pure gems.

## II. OCCURRENCE.

Beryllium occurs chiefly as the silicate, beryl,  $\text{Be}_3\text{Al}_2(\text{SiO}_2)_6$ , which contains 11-15% BeO. Emerald and aquamarine are of this formula. Gadolinite,  $\text{FeBe}_2\text{Y}_2\text{Si}_2\text{O}_{10}$  or  $\text{Be}_2\text{F}_3(\text{YO})_2(\text{SiO}_4)_2$ , 5-11% BeO; Leucophanite  $\text{NaBeFCa}(\text{SiO}_3)_2$ , 10-12% BeO; chrysoberyl,  $\text{Be}(\text{AlO}_2)_2$ , 19-20% BeO; euclase,  $\text{Be}(\text{AlOH})\text{SiO}_4$ , 17-18% BeO; Bertrandite,  $\text{Be}_2(\text{BeOH})_2\text{Si}_2\text{O}_7$ ,



40-43% BeO; and eudidymite,  $\text{HNaBeSi}_3\text{O}_8$ , 10-11% BeO, are other important minerals. Many other minerals<sup>(2,3)</sup> contain beryllium. Beryl was the source of material for this investigation.

### III. HISTORICAL.

In 1798, L. N. Vauquelin announced the discovery of a new earth, "la terre du Beril". He made the discovery in attempting to prove the identity of beryl and emerald, previously reported by Hauy, when he found that on boiling a solution of a precipitate previously supposed to be aluminium hydroxide in potassium hydroxide, that a portion of the precipitate was<sup>(4)</sup> thrown out of solution. The name proposed by Vauquelin was translated into the German as "Beryllerde" from whence came "Beryllium". The editors of Annales de Chimie suggested the name "glucine" because of the sweet taste of the fulfate, but later investigators have objected to the name because of the similarity to "glycine,"<sup>(5)</sup> and others because the sweetness is not peculiar to beryllium compounds alone, but is<sup>(6)</sup> possessed by the yttrium earths. Following the discovery of the element, Vauquelin studied and reported the properties of some of its compounds.<sup>(7,8,9,10)</sup> Berzelius,<sup>(12)</sup> Gay-Lussac,<sup>(11)</sup> and others also studied the known beryllium compounds, and prepared and reported others.

In 1828, Wohler<sup>(13)</sup> obtained metallic beryllium as a dark gray powder by reducing sublimed beryllium chloride with potassium in a platinum crucible. About the same time Bussy<sup>(14)</sup>







prepared impure beryllium by the same method.

(15)  
In 1842, Awdejew made the first determinations of the atomic weight of beryllium that have any claim to accuracy.

(16)  
Weeren (1854) published an extended and careful research on beryllium. He determined the atomic weight by the ratio  $\text{BeO}:\text{SO}_3$  in beryllium sulfate which he had carefully purified.

(17)  
In 1855, DeBray prepared metallic beryllium as a white metal, specific gravity 2.1, by the reduction of the chloride with sodium in a current of hydrogen. He describes the properties of the metal and of various compounds. Charles A. Joy, (18)  
published an extended bibliography of beryllium up to 1863.

He also published results on various methods of decomposing beryl and methods of separating aluminium and beryllium.

(19)  
Nilson and Petersson prepared beryllium by heating the chloride to bright redness with sodium in a sealed crucible.

(20)  
Kruss and Moraht reduced potassium beryllium fluoride with sodium. (21)  
Warren reports that he obtained beryllium by

electrolyzing fused beryllium bromide. This has since been declared a mistake by Parsons (3) who states that the bromide is not a conductor of electricity. Borchers (22)  
electrolyzed

(23)  
potassium ammonium beryllium fluoride. Lebeau obtained beryllium by electrolyzing sodium beryllium fluoride. A nickle crucible served as the cathode and a graphite anode was used. It was only necessary to melt the mass with a Bunsen



burner and then the current (6-7 amps, 35 volts) was sufficient to keep it molten.

This is a brief resume of the various methods used up to this time to prepare metallic beryllium.



## EXPERIMENTAL



#### IV. THE CRUDE MATERIAL.

The material used was beryl which is the only mineral of beryllium which contains enough beryllia to make its extraction practical. It is beryllium aluminium silicate,  $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$ , and contains 11-15%  $\text{BeO}$ . As impurities it contains iron, calcium, and magnesium. The beryl used came in lumps ranging in color from white to green with brown and blue streaks. It was prepared by crushing first with a sledge hammer, then thru a Blake jaw-crusher, where it was reduced to 1/16 inch. The material was then rotated in a ball mill for several days until it passed thru a 100-mesh sieve.

(24)

#### Analysis,

##### Composition of Beryl:

$\text{BeO}$	10. %
$\text{Al}_2\text{O}_3$	19. %
$\text{SiO}_2$	65.5%
$\text{Fe}_2\text{O}_3$	1.7 %
$\text{CaO}, \text{MgO}, \text{H}_2\text{O}$	3.8 % (by difference)
<hr/>	
	100. %

#### V. PARSON'S METHOD OF EXTRACTION.

One hundred grams of beryl were fused with an equal weight of sodium hydroxide in a nickel crucible, in a Case





furnace. The fused mass was broken up and just covered with water. Concentrated sulfuric acid was added in slight excess. The product of several fusions was treated in this way and then the whole mass was heated until fumes of sulfuric acid were given off. The residue now had the appearance of fine white powder. This residue was treated with hot water when the sulfates of beryllium, aluminium, iron and sodium passed into solution and were separated from the silica by filtration. The mother liquors were evaporated until the alums began to crystallize out, allowed to stand, and filtered from the alum. Most of the aluminium was separated in this way. The liquor from the alum was treated with nitric acid to convert all the iron present to the ferric condition, neutralized with ammonium hydroxide, and sufficient sodium acid carbonate added, in crystals, to saturate. The solution was warmed (50°C.) and shaken frequently for 24 hours. Most of the beryllium passed into solution almost free from aluminium and iron. By re-dissolving and treating the residue after filtration practically all of the beryllium was obtained in the bicarbonate solution. Ammonium sulfide was added to this solution to remove any iron that might have dissolved, and the solution filtered. The solution was diluted to ten times its volume and steam passed thru the liquid to the boiling point, which caused the beryllium to be precipitated as a fine, granular



basic carbonate,  $x\text{BeCO}_3$ ,  $y\text{Be}(\text{OH})_2$ . This is obtained quite pure<sup>(26)</sup> by filtering and washing. The yield was about 60% of the theoretical.

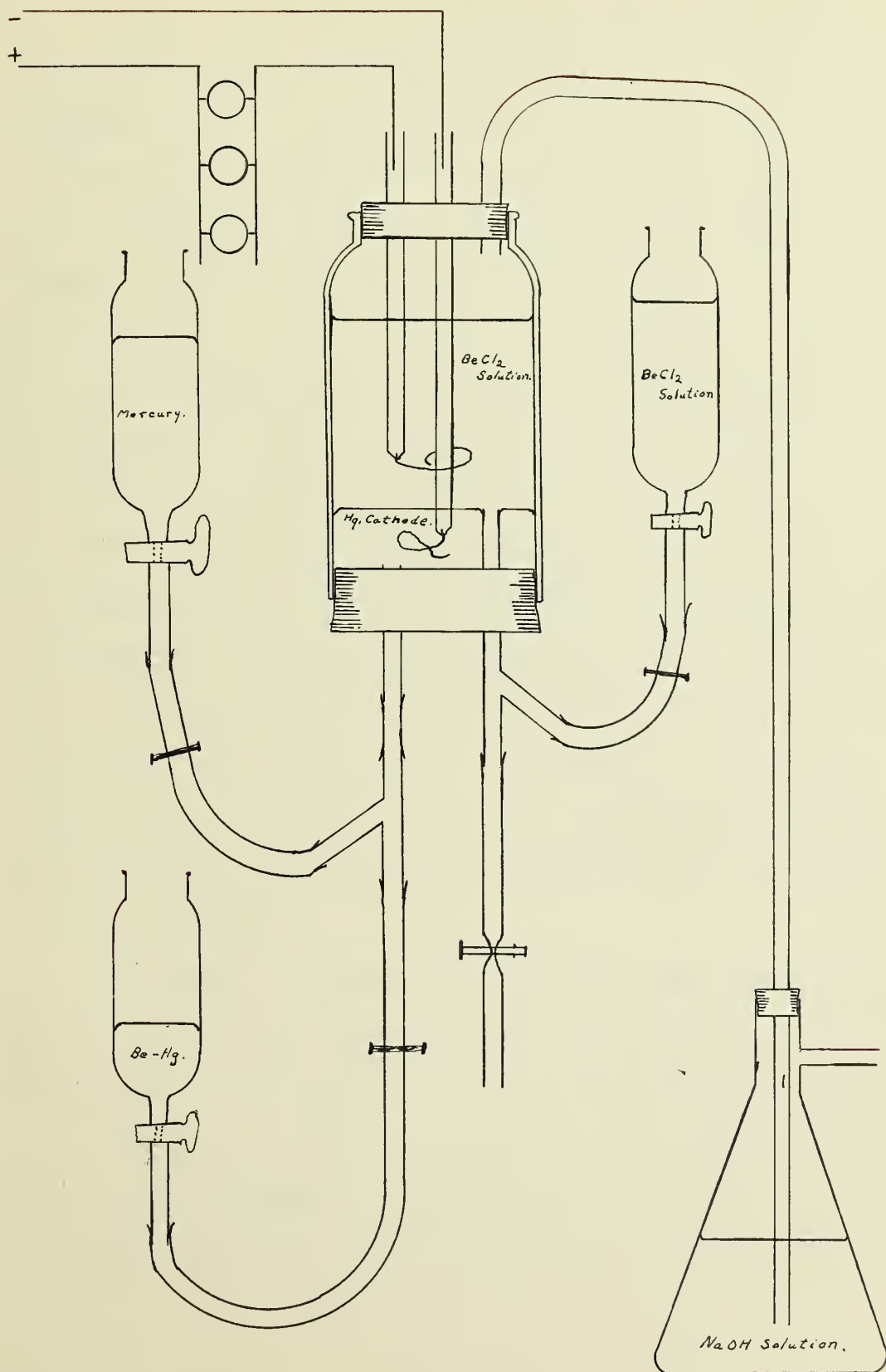
#### VI. PREPARATION OF BERYLLIUM CHLORIDE.<sup>(3,25)</sup>

The basic carbonate of beryllium as prepared above was dissolved in hydrochloric acid and evaporated to dryness. The residue was taken up in water and it was found that a few drops of concentrated hydrochloric acid were usually necessary to bring it into solution, due to the formation, on evaporation<sup>(5)</sup> of basic mixtures of various degrees of hydration.<sup>(25)</sup>

#### VII. ELECTROLYSIS OF BERYLLIUM CHLORIDE.

Several types of cell were tried but the cell finally used was of the nature of the accompanying drawing. The first cell was a 600cc. beaker equipped with a mercury cathode and a graphite anode. Connection was made to the mercury through a platinum wire sealed in a short length of glass tubing. Direct currents of 110 volts, and of 12 volts were tried. With the 110 volt circuit a bank of 12 lamps and a carbon rheostat resistance were inserted and varying resistances were tried. The graphite anode continually wore away under the action of the chlorine and settled on the amalgam from which it was separated by rolling in cloth. The crude cell did not give very satisfactory results and the cell as finally used was constructed









as follows:- The bottom of a 300 cc. bottle was removed and a rubber stopper substituted thru which were passed two lengths of glass tubing. One piece of tubing ended at the surface of the stopper and was used to draw off the amalgam and to introduce fresh mercury. This was accomplished by means of a Y connection (see figure) to which was attached two separatory funnels, one for the amalgam, the other for the mercury. The other piece of tubing terminated about 1/2 inch higher and was used to remove the electrolyzed solution and to introduce fresh aqueous beryllium chloride. The process was made more or less continuous, although not automatic, by connecting this tube, likewise, to two separatory funnels. Connection was made to the mercury cathode by means of a piece of glass tubing in which was sealed a short platinum wire. The tubing was filled with mercury to connect the wires from the source of current. The anode was a platinum wire similarly constructed, and distant from the cathode about 3 centimeters.

Experiments proceeded with varying resistances on both the 110 and 10 volt circuit. As finally tried the 10 volt circuit was used with a sufficient resistance to cause a current of 1-2 amperes to flow thru the cell. The electrolysis was not at all dependable. Concentration and resistance seemed to play an important part. At first the amalgam seemed to





form readily, but after a time equilibrium was reached and no more amalgam formed. At other times the beryllium salt hydrolyzed and had to be removed and converted to the chloride. With careful efforts to have the conditions the same the most unexpected reactions occurred and had to be overcome. Both aqueous and alcoholic <sup>(3)</sup> solutions of beryllium chloride were tried in an effort to easily obtain the amalgam but with very little difference in the result. The electrolysis is still unsatisfactory and merits continued research.

#### VIII. TREATMENT OF THE BERYLLIUM AMALGAM.

An effort was made to obtain metallic beryllium from the amalgam. The first plan suggested was to heat the amalgam in a stream of nitrogen. The beryllium amalgam was placed in a combustion tube in a furnace and the tube connected with a vacuum pump and a source of nitrogen. The nitrogen was prepared by drawing air slowly through ammonium hydroxide and then through a combustion tube containing copper oxide to decompose the ammonia into nitrogen and water, then thru another combustion tube containing copper gauze to remove the oxygen from the air. The gas was then drawn thru a long series of drying towers containing concentrated sulfuric acid; stick potassium hydroxide; and phosphorus pentoxide respectively.



The product obtained was yellow to gray in color and was probably a mixture of the oxide and occluded mercury. A supposition that the nitride might have formed seemed unlikely since the material did not decompose in boiling water, but dissolved in hydrochloric acid.

It was next decided to try to obtain beryllium from the amalgam in vacuum. The first trials were unsuccessful because the vacuum was not high enough. The metal oxidized and the product was white beryllium oxide.

Other attempts were made using a mercury pump by which vacuum of 0.001 mm. of mercury could be obtained and a gray powder was the result. After several such runs, the product which contained a little mercury was dissolved in hydrochloric acid, separated from the mercury, and precipitated as the hydroxide with ammonium hydroxide. This was filtered, washed, and dissolved in potassium hydroxide. Upon boiling beryllium hydroxide was again precipitated.



## CONCLUSIONS



## IX. SUMMARY.

Beryllium basic carbonate was obtained from beryl by the method suggested by Parsons. No attempt was made to get large yields but rather to obtain purity of product. The basic carbonate was converted to the chloride and the aqueous solution electrolyzed with a mercury cathode. This gave a beryllium amalgam. The amalgam was heated in vacuum to obtain metallic beryllium.

The investigation shows that beryllium amalgam may be formed by electrolyzing aqueous beryllium chloride. Metallic beryllium may be obtained by heating the amalgam in vacuum.

A new method of obtaining metallic beryllium was discovered.





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